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Theoretical Study of Oxidative Addition of Methane and Propane to Dihalobis(phosphine)palladium(II) Complexes PdX2(PH3)2 (X = F, Cl, Br, and I)

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Abstract

The possible routes of methane reactions with dihalobis(phosphine)palladium(II) complexes PdX2(PH3)2 (X = F, Cl, Br, and I), namely, electrophilic replacement of hydrogen, oxidative halogenation of methane, and oxidative addition of methane CH bonds to the palladium atom were considered. All the gas-phase reactions are thermodynamically unfavored and have an almost equal energy. The oxidative addition reaction was studied in detail: The geometry and relative stability of six diastereomeric reaction products, hydridomethyl palladium(IV) complexes CH3Pd(H)X2(PH3)2, were calculated. The most substantial structural features of the complexes and their relative stability are determined by relative arrangement of the hydrido and methyl ligands, having the strongest trans-effect, around the palladium atom. The endothermic effect of methane oxidative addition to the palladium complex increases in the order X = F < Cl < Br < I, which is connected with the increasing steric repulsion of the halo ligands in the most stable of the diastomeric reaction products. The energy of oxidative addition of secondary and primary CH bonds of propane to PdCl2(PH3)2 was calculated. The thermodynamic selectivity of the oxidative addition decreases in the order i-Pr > n-Pr > Me. The kinetic barriers of the methane reactions were calculated. The oxidative addition path was studied by the internal coordinate method. The oxidative addition is a concerted process with a late transition state. The results of the calculations are in qualitative agreement with experimental data.